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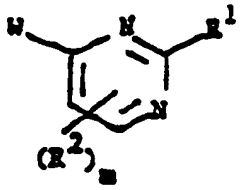
(54) Title: HERBICIDAL ARYL AND HETEROARYL PYRIMIDINES

(57) Abstract

This invention relates to novel aryl and heteroaryl pyrimidine derivatives, shown below, substituted at the 2- and 4-position of the pyrimidine ring, their use as herbicides and agricultural compositions comprising the same. In formula (I), W is a substituted phenyl or a substituted 5- or 6-membered aromatic heterocyclic ring wherein one or two atoms of said ring are selected from oxygen, nitrogen and sulfur; W being substituted by at least R; R is CO_2R^4, CHO, $CONH\text{-}O\text{-}CH_2CO_2R^4$, $COSR^4$, $CO_2CHR^5OCOR^6$ or $CH{=}NOR^4$; R^1, R^2, R^4, R^5, R^6 are as defined in the application; m = 1 or 2.



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HERBICIDAL ARYL AND HETEROARYL PYRIMIDINES

BACKGROUND OF THE INVENTION

This invention relates to novel substituted aryl and heteroaryl pyrimidines, their use as herbicides and agricultural compositions comprising the same.

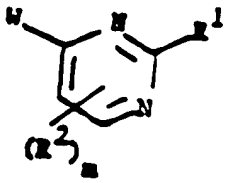
Various pesticidal aryl and heteroaryl pyrimidines are known. U.S. Patent No. 4,752,324 discloses 2-(2-alkyl-6-arylpyrimidin-4-yl)nicotinic acid derivatives having herbicidal activity. DE 40 31 798 describes fungicidal substituted pyridylpyrimidines. Furthermore, Harris et al. Aust. J. Chem., 1979, 32, 669-679, describes the plant growth regulating properties of diaryl heterocyclic compounds.

DESCRIPTION OF THE INVENTION

It has now been discovered that certain aryl and heteroaryl pyrimidines substituted at the 2 and 4-position of the pyrimidine ring exhibit herbicidal and plant growth regulating activity, when applied either pre or post emergence and used against annual and perennial grasses and broad leaf weeds.

The terms "herbicide" and "herbicidal" are used herein to denote the inhibitive control or modification of undesired plant growth. Inhibitive control and modification include all deviations from natural development such as, for example, total killing, growth retardation, defoliation, desiccation, regulation, stunting, tillering, stimulation, leaf burn, and dwarfing. The term "herbicidally effective amount" is used to denote any amount which achieves such control or modification when applied to the undesired plants themselves or to the area in which these plants are growing. The term "plants" is intended to include germinant seeds, emerging seedlings and established vegetation, including both roots and above-ground portions.

More particularly, this invention concerns compounds of the general formula I.



I

wherein W is a substituted phenyl or a substituted 5- or 6-membered aromatic heterocyclic ring wherein one or two atoms of said ring are selected from oxygen, nitrogen and sulfur; W being substituted by at least R;

R is CO_2R^4, CHO, $CONH\text{-}O\text{-}CH_2CO_2R^4$, $COSR^4$, $CO_2CHR^5OCOR^6$ or $CH{=}N\text{-}OR^4$;

R^1 is Ar, $(Z)_xY\text{-}Ar$, or ZAr wherein Ar is an optionally substituted aryl or heteroaryl group selected from the group consisting of phenyl, pyridyl, piperonyl, naphthyl, indolyl, quinolyl, isoquinolyl, quinoxalinyl, quinazolinyl, benzoxazolyl, benzothiazolyl, phenanthryl, pyridyl-N-oxide, anthranilyl, pyrimidinyl, pyrazinyl, thienyl, furyl, pyrrolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, imidazolyl, pyrazolyl, oxadiazolyl and thiadiazolyl wherein the optional substituents are phenoxy, halo, alkyl, alkenyl, haloalkyl, haloalkylthio, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, haloalkoxy, alkoxyalkyl, cyano, nitro, alkoxycarbonyl, amino, alkylamino, dialkylamino, hydroxy, Y is O, S or NH; Z is an optionally substituted C_1-C_3alkyl, C_2-C_4alkynyl or an optionally substituted C_2-C_4alkenyl, wherein the substituents are independently alkyl and halogen, x is 0 to 2;

R^2 is independently hydrogen, halogen, alkyl, alkenyl, haloalkyl, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, alkoxyalkyl, cyano, nitro, amino, alkylamino, dialkylamino, CO_2R^4 and hydroxy, m is 1 to 2;

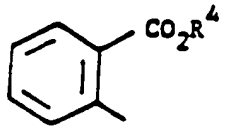
R^4 is hydrogen, alkali or alkaline earth cation, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium

cation, trialkylsulfoxonium cation, alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl;

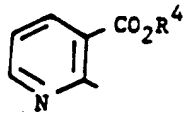
R^5 is hydrogen or alkyl; and

R^6 is alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl;

provided that (i) when R^1 is phenyl; W is not



and (ii) when R^1 is optionally substituted phenyl and W is



R^2 is not alkyl or alkenyl.

The term "alkyl" as used herein includes straight, branched and cyclo alkyl groups, preferably containing up to 6 carbon atoms. This applies to alkyl moieties contained for example, in "haloalkyl" and each alkyl group of "alkoxyalkyl". The term "alkenyl is represented by 2 to 6 carbon atoms.

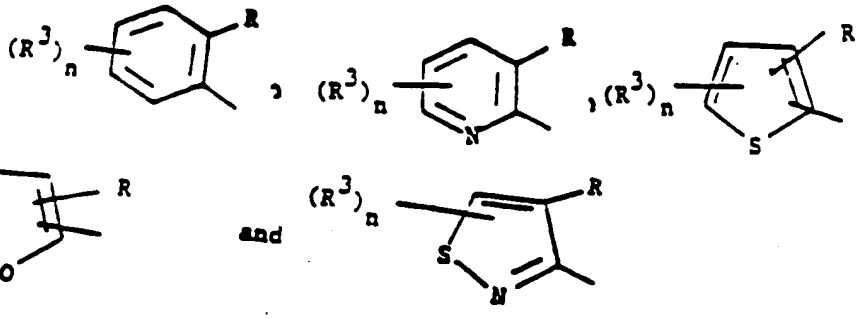
Suitable halogen groups include fluorine, chlorine, bromine, and iodine. Haloalkyl groups may be substituted by one or more halogen atoms. The term "alkali cation" is defined as metals of group 1A of the periodic chart and particularly include sodium and potassium. The term "alkaline earth cation" includes magnesium, calcium, strontium and barium.

The term "phenylalkyl" refers to an alkyl group substituted with a phenyl. The terms "optionally substituted phenyl", "optionally substituted phenylalkyl" and "optionally substituted phenoxy" refers to a phenyl, phenylalkyl, or phenoxy group substituted at one or more of the ring carbon atoms with a group selected from alkyl, haloalkyl, halogen,

alkoxy, alkenyl, cyano, and nitro.

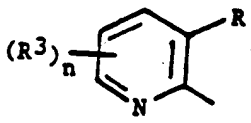
The term "substituted ammonium cation" refers to an ammonium cation substituted by a C_1-C_{20}alkyl, di-C_1-C_{20}alkyl, tri-C_1-C_{20}alkyl, tetra-C_1-C_{20}alkyl, hydroxy-C_1-C_5alkyl, di(hydroxy-C_1-C_5alkyl), tri(hydroxy-C_1-C_5alkyl), C_{1-5}alkoxyC_1-C_5alkyl, hydroxy-C_1-C_5alkoxy-C_1-C_5alkyl or C_1-C_5alkoxycarbonyl-C_1-C_5alkyl group.

A preferred sub-group of compounds of formula I are compounds wherein W is phenyl, pyridyl, thienyl, furyl or isothiazolyl.

W is preferably  and

wherein R^3 is independently hydrogen, halogen, alkyl, haloalkyl, alkoxy, cyano, alkoxycarbonyl, alkylamino, dialkylamino and -N(R^5)-CO-R^6, and n is 1 to 4.

A particularly preferred subgroup of compounds of formula I are compounds wherein

(i) W is  ;

(ii) R is CO_2R^4, CHO, CONH-O-$CH_2CO_2R^4$, $COSR^4$, $CO_2CHR^5OCOR^6$ or $CH=NOR^4$;

(iii) R^1 is Ar, $(Z)_xYAr$ or ZAr wherein Ar is an optionally substituted phenyl,

pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl, anthranilyl or phenanthryl; Y is O, S or NH; Z is an optionally substituted C_1-C_3alkyl, C_2-C_4alkynyl or optionally substituted C_2-C_4alkenyl wherein the substituents are independently alkyl and halogen and x is 0 to 2;

(iv) R^2 is hydrogen, CO_2R^4 and alkoxy;

(v) R^3 is hydrogen and halogen.

(vi) R^4 is hydrogen, alkali or alkaline earth cation, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium cation, trialkylsulfoxonium cation, alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl;

(vii) R^5 is hydrogen or alkyl; and

(viii) R^6 is alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl.

Preferably R is $CO_2CHR^5OCOR^6$ or CO_2R^4 wherein R^4 is hydrogen, alkyl, alkali or alkaline earth cations, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium cation, or trialkyl sulfoxonium cation and

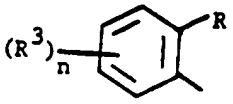
R^1 is optionally substituted phenyl, pyridyl, naphthyl, quinolyl, piperonyl, $(Z)_x$Ophenyl and (Z)phenyl wherein Z is C_1-C_3alkyl, C_2-C_4alkynyl or C_2-C_4alkenyl and x is 1.

More prefreably R is CO_2R^4 wherein R^4 is hydrogen, Na, NH_4, K, Ca, Mg, trimethyl sulfonium, trimethyl sulfoxonium and isopropyl ammonium; and

R^1 is phenyl or substituted phenyl wherein the substituents are independently methyl, methoxy, chloro, fluoro, amino, haloalkoxy, nitro and haloalkyl; and

R^2 is hydrogen, alkoxy, or CO_2R^4.

Another particularly preferred subgroup of compounds of formula I are compounds wherein

(i) W is  ;

(ii) R is CO_2R^4, CHO, $CONH\text{-}O\text{-}CH_2CO_2R^4$, $COSR^4$, $CO_2CHR^5OCOR^6$ or $CH{=}NOR^4$;

(iii) R^1 is Ar, $(Z)_xYAr$ or ZAr wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl, anthranilyl or phenanthryl; Y is O, S or NH; Z is an optionally substituted C_1-C_3alkyl, C_2-C_4alkynyl or optionally substituted C_2-C_4alkenyl wherein the substituents are independently alkyl and halogen and x is 0 to 2;

(iv) R^2 is hydrogen, CO_2R^4, alkoxy and alkyl;

(v) R^3 is hydrogen and halogen and n is 1 or 2;

(vi) R^4 is hydrogen, alkali or alkaline earth cation, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium cation, trialkylsulfoxonium cation, alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl;

(vii) R^5 is hydrogen or alkyl; and

(viii) R^6 is alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl and optionally substituted phenylalkyl.

Preferably R is $CO_2CHR^5OCOR^6$ or CO_2R^4 wherein R^4 is hydrogen, alkyl, alkali or alkaline earth cations, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium cation, or trialkyl sulfoxonium cation and

R^1 is optionally substituted phenyl, pyridyl, naphthyl, quinolyl, piperonyl, $(Z)_x$Ophenyl and (Z)phenyl wherein Z is C_1-C_3alkyl, C_2-C_4alkynyl or C_2-C_4alkenyl and x is 1.

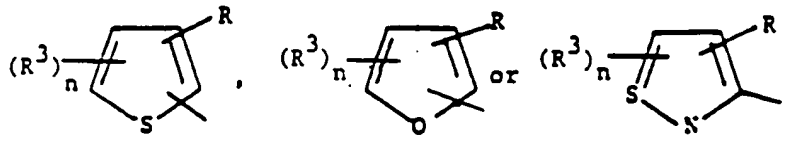
More preferably R is CO_2R^4 wherein R^4 is hydrogen, Na, NH_4, K, Ca, Mg, trimethyl sulfonium, trimethyl sulfoxonium and isopropyl ammonium; and

R^1 is phenyl or substituted phenyl wherein the substituents are independently methyl, methoxy, chloro, fluoro, amino, haloalkoxy, nitro and haloalkyl and R^3 is halogen.

Another preferred sub group of compounds of Formula I include the compounds wherein R is CO_2R^4; R^4 is hydrogen, Na, NH_4, K, Ca, Mg, trimethylsulfonium, trimethylsulfoxonium or isopropylammonium; R^1 is Ar, $(Z)_xY$-Ar and ZAr wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl or phenanthryl wherein the optional substituents are halo, alkyl, alkenyl, haloalkyl, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, haloalkoxy, alkoxyalkyl, cyano, nitro, alkoxycarbonyl, amino, alkylamino, dialkylamino and hydroxy; Y is O, S or NH, preferably O; Z is an optionally substituted C_1-C_3alkyl, C_2-C_4alkynyl or an optionally substituted C_2-C_4alkenyl wherein the substituents are independently alkyl and halogen; and x is 0 to 2.

Still another preferred subgroup of compounds of Formula I include the compounds

wherein W is



R is CO_2R^4; CHO; $CONH\text{-}O\text{-}CH_2CO_2R^4$; $COSR^4$; $CO_2CHR^5OCOR^6$ or $CH{=}NOR^4$;

R^1 is Ar, Z_xOAr or ZAr wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl or phenanthryl;

R^2 is hydrogen; and

R^3 is hydrogen and halogen.

In another embodiment the invention includes a herbicidal composition comprising a herbicidally effective amount of a compound of Claim 1 in association with an agriculturally acceptable diluent.

A general process for making the compounds of this invention is as follows.

Appropriately substituted 1-(aryl or heteroaryl)-3-(N,N-dimethylamino)prop-2-en-1-one is heated with an appropriately substituted amidine or amidine hydrochloride and a (optional) base, such as sodium methoxide, in a suitable solvent, such as methanol, to afford the substituted 4-(aryl or heteroaryl)pyrimidine.

The substituted amidines used in this process were either purchased or prepared from commercially available starting materials. For example, the procedure of R.S.Garigipati (*Tetrahedron Letters*, 31, 1969 (1990)) was used to prepare amidines from the appropriately substituted nitrile by reaction with chloromethylaluminum amide in toluene.

The process for making the compounds of this invention will be more fully understood by reference to the following examples.

EXAMPLE 1

a) Preparation of 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one.

A suspension of 27.1 g (164 mmol) 2-acetylpyridine-3-carboxylic acid in 200 mL toluene is heated to reflux to remove water by azeotropic distillation. After approximately 20 mL of distillate is collected, the solution is cooled to ambient temperature and 54 mL N,N-dimethylformamide dimethylacetal is added dropwise. The brown solution is heated to reflux for 5 h, allowed to cool and concentrated to low volume *in vacuo*. This solution is treated with diethyl ether and stirred overnight. The orange crystals (mp 126-129°C) are collected by vacuum filtration. The ^{1}H NMR and mass spectra are consistent with 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one.

b) Preparation of 2-[4-(2-phenyl)pyrimidinyl]-3-pyridinecarboxylic acid (Compound 7 in Table 1).

To a solution of 2.00 g (8.54 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one and 1.50 g (8.54 mmol) benzamidine hydrochloride hydrate in 100 mL anhydrous methanol, is added 4.0 mL 25% sodium methoxide in methanol. The resulting dark solution is refluxed for 6 h allowing about half of the methanol to distill off, then stirred at ambient temperature for 72 h and evaporated to dryness *in vacuo*. The residue is partitioned between ethyl acetate and 0.5 M aqueous sodium hydroxide. The aqueous layer is washed once with ethyl acetate and acidified to pH 3 with concentrated HCl. The solid precipitate is collected by vacuum filtration and dried *in vacuo* at 50°C for 1 h to yield a tan solid, m.p. 169-170°C. The ^{1}H NMR and mass spectra are consistent with the desired 2-[4-(2-phenyl)pyrimidinyl]-3-pyridine-carboxylic acid.

c) Preparation of 2-[4-(2-phenyl)pyrimidinyl]-3-pyridinecarboxylic acid, monosodium salt (Compound 1 in Table 1).

To a slurry of 1.00 g (3.61 mmol) 2-[4-(2-phenyl)pyrimidinyl]-3-pyridinecarboxylic acid in 10 mL methanol, is added 0.82 mL (3.61 mmol) 25% sodium methoxide in methanol. The solution is stirred for 5 min and evaporated *in vacuo* to yield a solid foam. The ^{1}H NMR and mass spectra are consistent with the 2-[4-(2-phenyl)pyrimidinyl]-3-pyridinecarboxylic acid, monosodium salt.

EXAMPLE 2

a) Preparation of 2-[4-[2-(3-chlorophenyl)]pyrimidinyl]-3-pyridinecarboxylic acid (Compound 14 in Table 1).

To a solution of 4.29 g (18.32 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one and 3.50 g (18.32 mmol) 3-chlorobenzamidine hydrochloride in 150 mL methanol, is added 8.5 mL 25% sodium methoxide in methanol. The resulting brown solution is refluxed for approximately 6 h allowing about half of the methanol to distill off, then allowed to cool, and evaporated *in vacuo*. The residue is partitioned between water and ethyl acetate. An insoluble solid is collected by vacuum filtration. This solid is dissolved in 1 M aqueous sodium hydroxide and acidified to pH 3 with concentrated HCl. The resulting precipitate is collected by vaccum filtration and dried to yield a tan solid (mp 163-166°C). The ^{1}H NMR and mass spectra are consistent with those expected for 2-[4-[2-(3-chlorophenyl)]pyrimidinyl]-3-pyridinecarboxylic acid.

EXAMPLE 3

Preparation of 2-[4-[2-(4-fluorophenyl)]pyrimidinyl]-3-pyridinecarboxylic acid (Compound 16 in Table 1).

To a solution of 5.88 g (25.1 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-

dimethylamino)prop-2-en-1-one and 3.47 g (25.1mmol) 4-fluorobenzamidine in 150 mL methanol is added 12.1 mL (53 mmol) 25% sodium methoxide in methanol. The solution is stirred and heated to reflux allowing some of the methanol to distill off. After 2 hours, the heat is turned off and the reaction is stirred at room temperature overnight.

The solution is refluxed for another 4 hours with removal of the distillate. The reaction is cooled and evaporated *in vacuo*. The residue is taken up in water and washed twice with ethyl acetate. A solid precipitate is formed in the ethyl acetate wash and collected by vacuum filtration. The solid is dissolved in 1 M NaOH, and acidified with concentrated HCl. The resulting solid is collected by vacuum filtration. After drying *in vacuo*, a white solid is obtained (m.p. 194-196°C).

The original aqueous layer is acidified with concentrated HCl and the solid is collected by vacuum filtration. This solid is recrystalized from ethyl acetate to afford light tan crystals (m.p. 195-196°C). The ^{1}H NMR and mass spectra of both solids are identical and consistent with the desired 2-[4-[2-(4-fluorophenyl)]pyrimidinyl]-3-pyridinecarboxylic acid.

EXAMPLE 4

Preparation of 2-[4-[2-(3-chloro-4-methylphenyl)]pyrimidinyl]-3-pyridinecarboxylic acid (Compound 24 in Table 1).

To a solution of 3.47 g (14.8 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one and 2.50 g (14.8 mmol) 3-chloro-4-methylbenzamidine in 150 mL methanol, is added 6.8 mL 25% sodium methoxide in methanol. The resulting solution is refluxed for 2 hours allowing about half of the methanol to distill off and stirred at ambient temperature over a weekend. Refluxing is continued for 4 additional hours, the mixture is cooled and evaporated *in vacuo*. The residue is treated with 1 M aqueous sodium hydroxide and filtered to remove an insoluble solid. The filtrate is washed with ethyl acetate, acidified to pH 3 with concentrated HCl, and extracted with 3

portions of ethyl acetate, which upon evaporation *in vacuo*, afforded a tan solid. The insoluble solid obtained from the initial filtration is suspended in 1 M aqueous sodium hydroxide at 50°C until dissolution, washed with ethyl acetate, filtered, and acidified with concentrated HCl. The resulting aqueous solution is extracted with 2 portions of ethyl acetate. The ethyl acetate extracts are washed with water, dried over magnesium sulfate, filtered, and evaporated *in vacuo* to give a light tan solid, which is combined with the 0.20 g of tan solid obtained above. The ^{1}H NMR and mass spectra of this combination (mp 168-172°C) are consistent with the desired 2-[4-[2-(3-chloro-4-methylphenyl)]pyrimidinyl]-3-pyridinecarboxylic acid.

EXAMPLE 5

Preparation of 2-[4-[2-(3-chlorophenoxy)methyl]pyrimidinyl]-3-pyridinecarboxylic acid (Compound 22 in Table 1).

To a solution of 2.66 g (11.4 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one and 2.10 g (11.4 mmol) 3-chlorophenoxyacetamidine in 100 mL methanol, is added 5.2 mL (22.8 mmol) 25% sodium methoxide in methanol. The resulting solution is gently refluxed overnight allowing about half of the methanol to distill off. The reaction mixture is evaporated *in vacuo* and the residue is partitioned between 0.5 M aqueous sodium hydroxide and ethyl acetate. The aqueous layer is washed with ethyl acetate, then acidified to pH 3 with concentrated HCl. The crude solid product is collected by vacuum filtration and purified by silica gel chromatography (2:1 ethyl acetate: methanol) to afford a tan solid (mp 155-158°C). The ^{1}H NMR and mass spectra of this solid are as expected for 2-[4-[2-(3-chlorophenoxy)methyl]-pyrimidinyl]-3-pyridinecarboxylic acid.

EXAMPLE 6

Preparation of 2-[4-[2-(2-Phenyl)ethenyl]pyrimidine]-3-pyridinecarboxylic acid (Compound 26 in Table 1).

To a solution of 2.72 g (11.6 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one and 1.86 g (11.6 mmol) cinnamamidine in 50 mL methanol, is added 8.0 mL 25% sodium methoxide in methanol. The resulting dark solution is refluxed for 2 hours with removal of the distillate. After stirring at ambient temperature for 72 hours, the reaction mixture is treated with 2.0 mL acetic acid and evaporated to dryness *in vacuo*. The residue is partitioned between saturated aqueous sodium bicarbonate and ethyl acetate. The aqueous layer is washed with two portions of ethyl acetate, acidified to pH 4 with concentrated HCl and filtered to remove crude solid product. The filtrate is extracted with ethyl acetate and evaporated *in vacuo* to yield a brown oil. The crude solid is combined with the brown oil and purified by thin layer preparatory chromatography on silica gel with 180:20:1 dichloromethane: methanol:acetic acid to afford a tan solid (mp 167°C decomposition). The ^{1}H NMR spectrum of this solid is as expected for 2-[4-[2-(2-phenyl)ethenyl]pyrimidinyl]-3-pyridinecarboxylic acid.

EXAMPLE 7

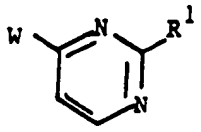
Preparation of 2-[4-[2-(1-naphthyl)]pyrimidinyl]-3-pyridinecarboxylic acid (Compound 27 in Table 1).

To a solution of 4.46 g (19 mmol) 1-(3-methoxycarbonylpyridin-2-yl)-3-(N,N-dimethylamino)prop-2-en-1-one and 3.24 g (19 mmol) 1-naphthamidine in 50 mL methanol, is added 13 mL (57 mmol) 25% sodium methoxide in methanol. The resulting dark solution is refluxed for 18 hours. The reaction mixture is treated with 3.3 mL acetic acid and evaporated *in vacuo*. The residue is chromatographed on silica gel with 4:1 ethyl acetate:methanol. The product containing fractions are evaporated *in vacuo*, suspended in ethyl acetate, filtered and evaporated *in vacuo* to yield slightly impure product. This solid

is rechromatographed on silica gel with 90:10:1 ethyl acetate:methanol:acetic acid to finally afford a tan solid (mp 205-207°C). The ^{1}H NMR spectrum of this solid is as expected for 2-[4-[2-(1- naphthyl)]-pyrimidinyl]-3pyridinecarboxylic acid.

These and other compounds which can be made by the foregoing processes are set forth in Tables 1 and 2 which follow, wherein the various substituent groups are indicated.

TABLE 1



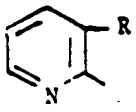
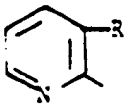
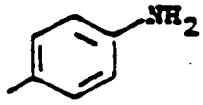
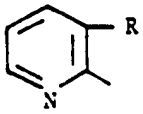
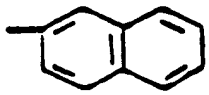
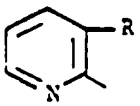
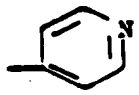
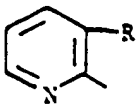
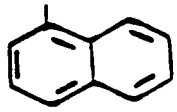
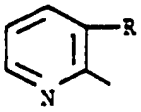
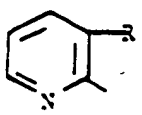
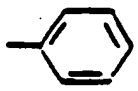
Cpd #	W	R	R¹	m.p.°C
1		$-CO_2^-Na^+$		>270
2		CO_2H		192.5-196
3		$CO_2^-Na^+$		260 (decomp.)
4		CO_2H		287-289
5		$CO_2^-Na^+$		125 (decomp.)
6		$CO_2^-Na^+$		284 (decomp.)
7		CO_2H		169-170

TABLE 1 (cont)

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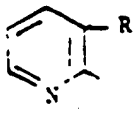
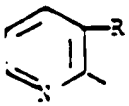
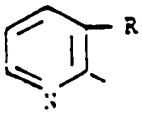
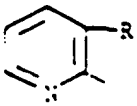
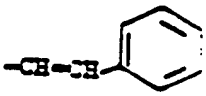
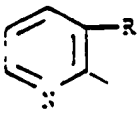
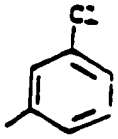
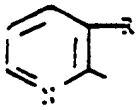
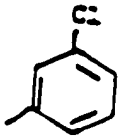
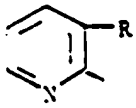
8		$CO_2^-Na^+$		>270
9		$-C(=O)-NH-OCH_2CO_2CH_3$		134-140.5
10		CO_2H		185 (decomp.)
11		$CO_2^-Na^+$		>300
12		$CO_2^-Na^+$		265 (decomp.)
13		CO_2CH_3		118-119
14		CO_2H		163-166
15		$CO_2^-Na^+$		>280

TABLE 1 (cont)

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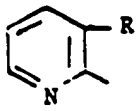
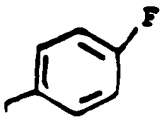
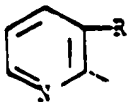
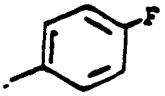
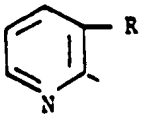
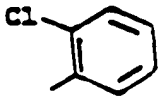
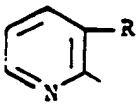
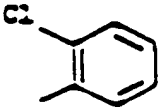
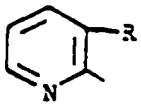
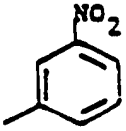
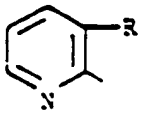
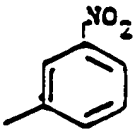
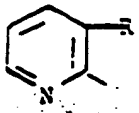
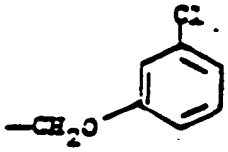
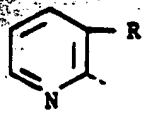
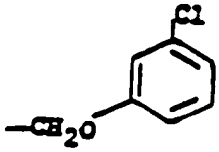
16		CO_2H		195-196
17		$CO_2^-Na^+$		>280
18		CO_2H		160-163
19		$CO_2^-Na^+$		64.5-123.5
20		CO_2H		235-237 (decomp.)
21		$CO_2^-Na^+$		282 (decomp.)
22		CO_2H		155-158
23		$CO_2^-Na^+$		245-251

TABLE 1 (cont)

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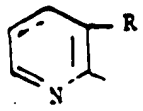
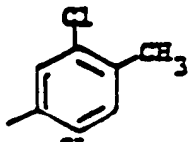
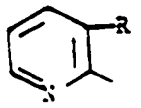
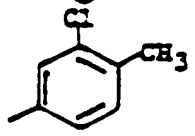
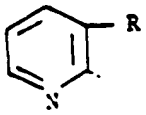
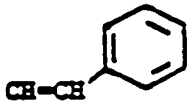
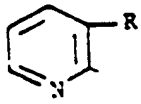
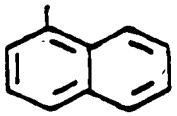
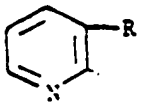
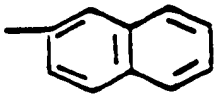
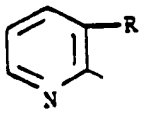
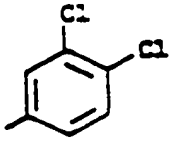
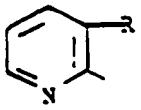
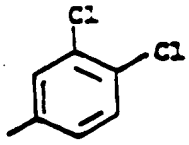
24		CO_2H		168-172
25		$CO_2^-Na^+$		>280
26		CO_2H		183-186
27		CO_2H		205-207
28		CO_2H		156-162
29		CO_2H		194-195
30		$CO_2^-Na^+$		>280

TABLE 1 (cont)

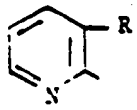
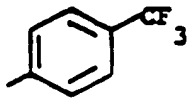
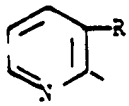
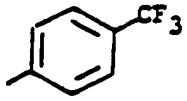
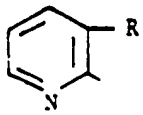
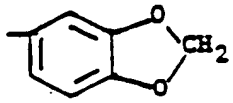
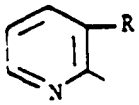
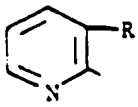
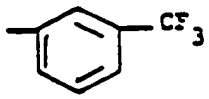
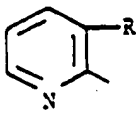
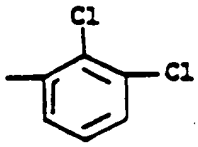
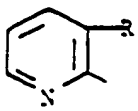
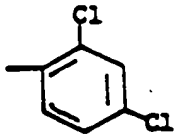
Cpd #	W	R	R'	m.p.°C
31		CO_2H		233-237
32		$CO_2^-Na^+$		>280
33		CO_2H		212-216
34		CO_2H		170-172
35		CO_2H		
36		CO_2H		75 (decomp.)
37		CO_2H		115

TABLE 1 (cont)

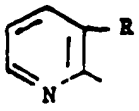
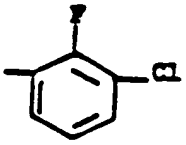
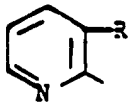
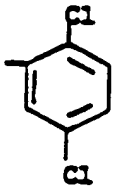
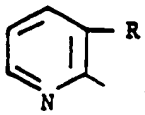
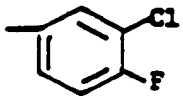
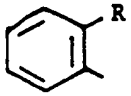
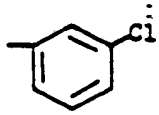
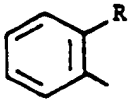
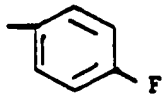
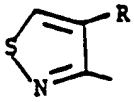
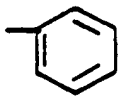
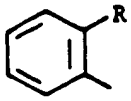
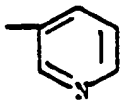
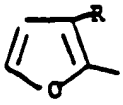
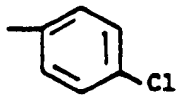
Cpd #	W	R	R'	m.p.°C
38		CO_2H		169.5-175.5
39		CO_2H		85-93
40		CO_2H		205-212
41		CO_2H		
42		CO_2H		
43		CO_2H		
44		CO_2H		
45		CO_2H		

TABLE 1 (cont)

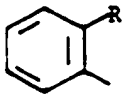
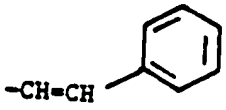
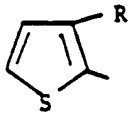
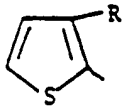
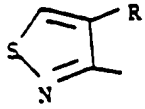
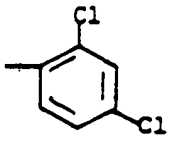
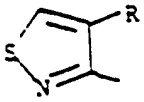
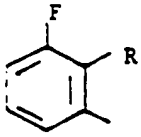
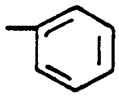
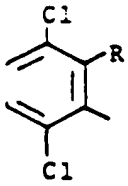
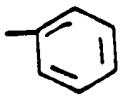
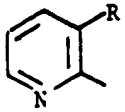
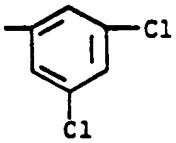
Cpd #	W	R	R¹	m.p.°C
46		CO_2H		
47		CO_2H		
48		CO_2H		
49		$CO_2^-Na^+$		
50		CO_2H		
51		CO_2H		
52		CO_2H		
53		CO_2H		218-221

TABLE 1 (cont)

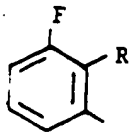
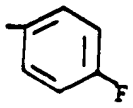
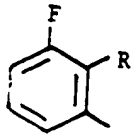
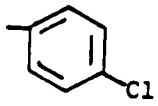
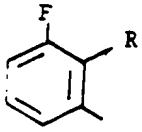
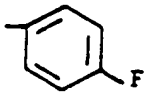
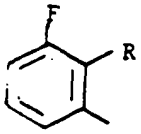
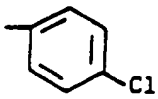
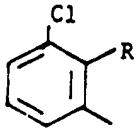
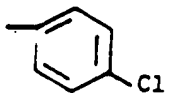
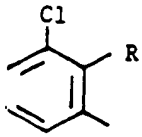
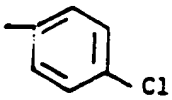
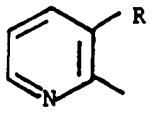
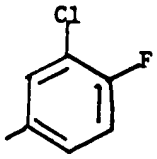
Cpd #	W	R	R'	m.p.°C
54		$CO_2^-Na^+$		>300
55		$CO_2^-Na^+$		>300
56		CO_2H		154-167
57		CO_2H		213-214
58		CO_2H		169-173
59		$CO_2^-Na^+$		>300
60		$CO_2^-Na^+$		210-217

TABLE 1 (cont)

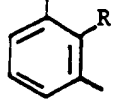
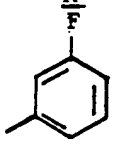
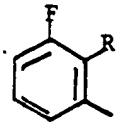
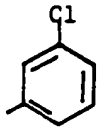
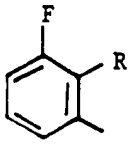
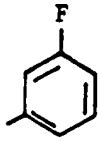
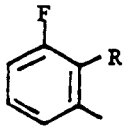
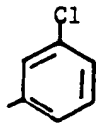
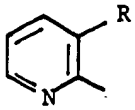
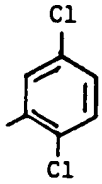
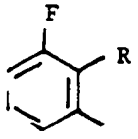
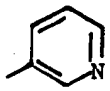
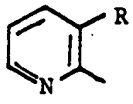
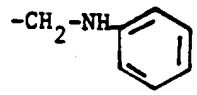
Cpd #	W	R	R'	m.p.°C
61		CO_2H		127-134
62		CO_2H		118-127
63		$CO_2^-Na^+$		>300
64		$CO_2^-Na^+$		>300
65		$CO_2^-Na^+$		185-195
66		$CO_2^-Na^+$		>300
67		CO_2H		238-240

TABLE 1 (cont)

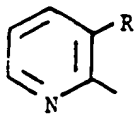
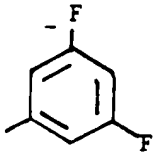
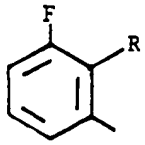
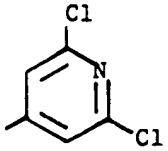
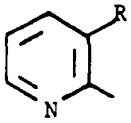
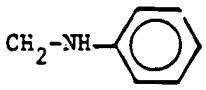
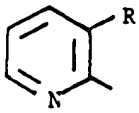
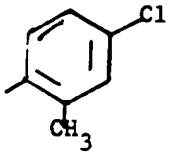
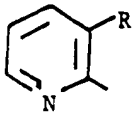
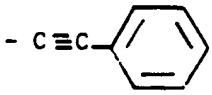
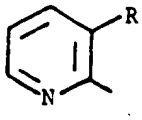
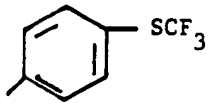
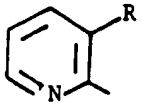
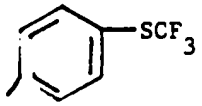
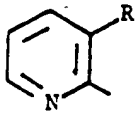
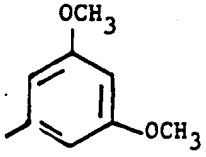
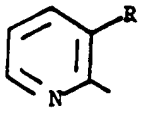
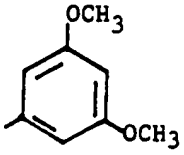
Cpd #	W	R	R^1	m.p.°C
68		$CO_2^-Na^+$		>260
69		$CO_2^-Na^+$		176 (decomp)
70		$CO_2^-Na^+$		>250
71		$CO_2^-Na^+$		267.50 (decomp)
72		$CO_2^-Na^+$		
73		CO_2H		210-215
74		$CO_2^-Na^+$		>290
75		CO_2H		90-92
76		$CO_2^-Na^+$		>250

TABLE 1 (cont)

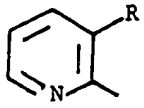
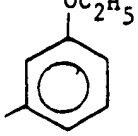
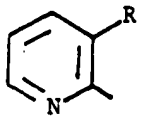
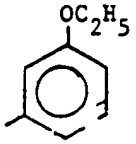
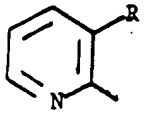
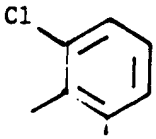
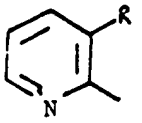
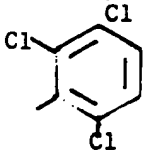
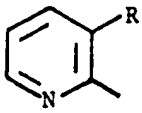
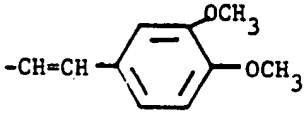
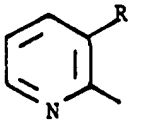
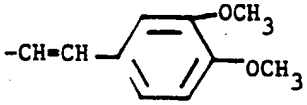
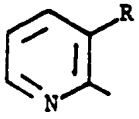
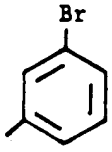
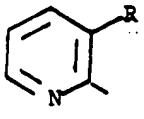
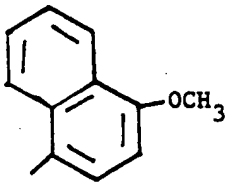
Cpd #	W	R	R'	m.p.°C
77		CO_2H		138-140
78		$CO_2^-Na^+$		210-212
79		CO_2H		243.5-247
80		$CO_2^-Na^+$		>300
81		CO_2H		107-110
82		$CO_2^-Na^+$		>300
83		$CO_2^-Na^+$		>300
84		CO_2H		138-141

TABLE 1 (cont)

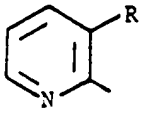
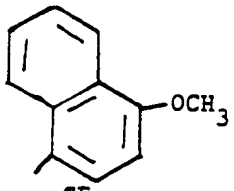
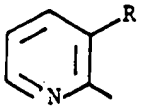
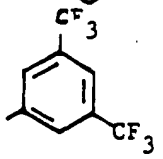
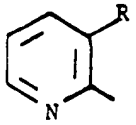
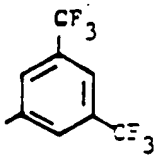
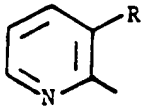
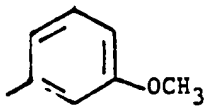
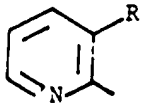
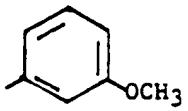
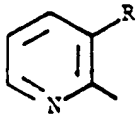
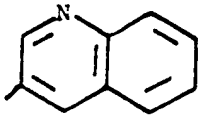
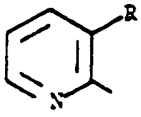
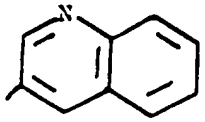
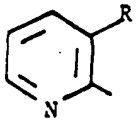
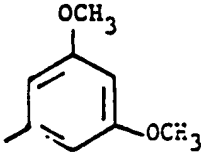
Cpd #	W	R	R'	m.p.°C
85		$CO_2^-Na^+$		>300
86		CO_2H		180-182
87		$CO_2^-Na^+$		>300
88		CO_2H		95-98
89		$CO_2^-Na^+$		250-252
90		CO_2H		131-133
91		$CO_2^-Na^+$		>300
92		CO_2H		264.5-271

TABLE 1 (cont)

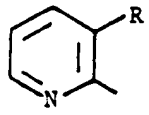
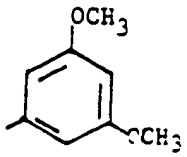
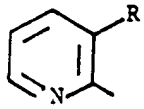
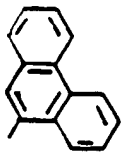
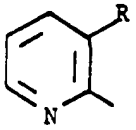
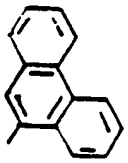
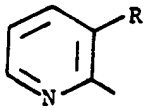
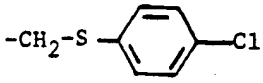
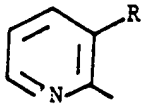
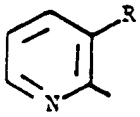
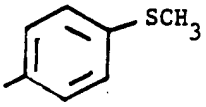
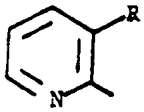
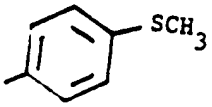
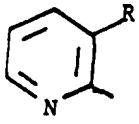
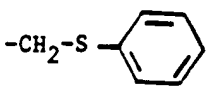
Cpd #	W	R	R'	m.p.°C
93		$CO_2^-Na^+$		>300
94		CO_2H		95-97
95		$CO_2^-Na^+$		222-225
96		CO_2H		86.5-91.5
97		$CO_2^-Na^+$		288.5-291.5
98		CO_2H		211-213
99		$CO_2^-Na^+$		>300
100		CO_2H		oil

TABLE 1 (cont)

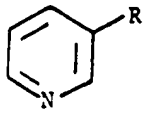
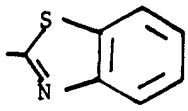
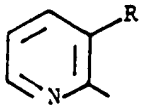
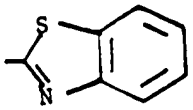
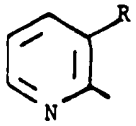
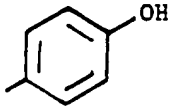
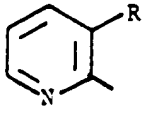
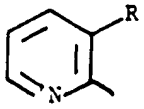
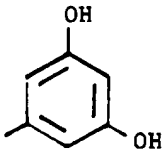
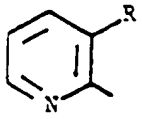
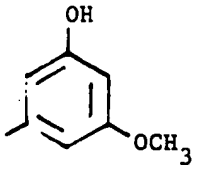
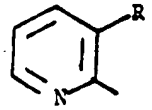
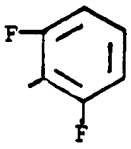
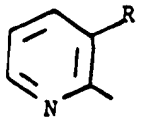
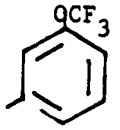
Cpd #	W	R	R'	m.p.°C
101		CO_2H		269-270
102		$CO_2^-Na^+$		>300
103		$CO_2^-Na^+$		>275
104		$CO_2^-Na^+$		>290
105		$CO_2^-Na^+$		>300
106		$CO_2^-Na^+$		>300
107		$CO_2^-Na^+$		235
108		$CO_2^-Na^+$		278-281

TABLE 1 (cont)

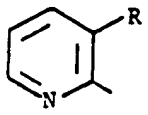
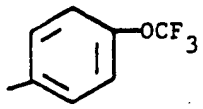
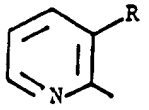
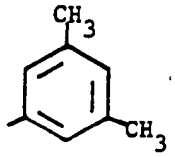
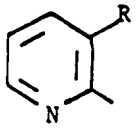
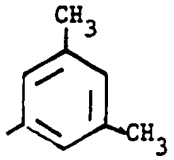
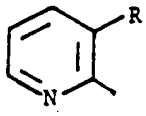
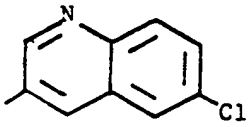
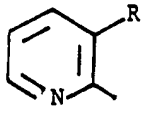
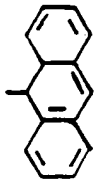
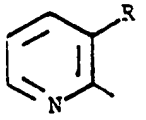
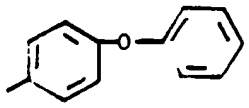
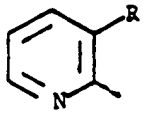
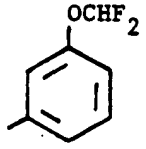
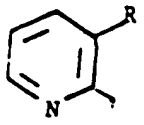
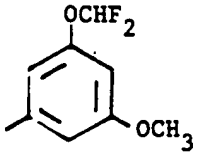
Cpd #	W	R	R'	m.p.°C
109		$CO_2^-Na^+$		>290
110		CO_2H		209.5-213.5
111		$CO_2^-Na^+$		>300
112		$CO_2^-Na^+$		>300
113		$CO_2^-Na^+$		233-236
114		$CO_2^-Na^+$		> 300
115		$CO_2^-Na^+$		115-119
116		$CO_2^-Na^+$		244 (decomp)

TABLE 1 (cont)

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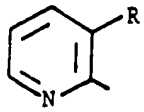
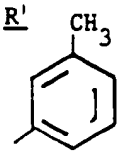
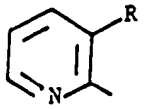
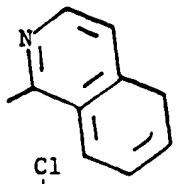
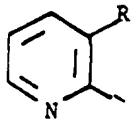
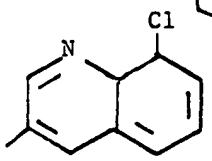
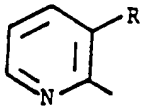
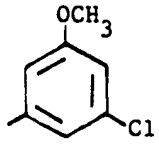
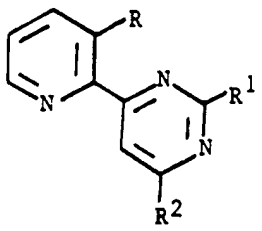
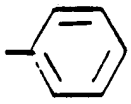
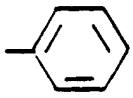
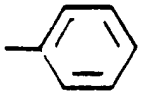
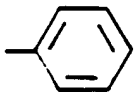
117		$CO_2^-Na^+$		278.5-281
118		$CO_2^-Na^+$		>250
119		$CO_2^-Na^+$		>250
120		$CO_2^-Na^+$		>290

TABLE 2



Cpd #	R	R^2	R^1	m.p.°C
121	$CO_2^-Na^+$	OH		
122	$CO_2^-Na^+$	$-CO_2^-Na^+$		
123	$CO_2^-Na^+$	$-OC_2H_5$		
124	$CO_2^-Na^+$	OCH_3		
125	$CO_2^-Na^+$	$-OC_2H_5$		

EXAMPLE 8

The test compounds are weighed and dissolved in a stock solution consisting of acetone:deionized water (1:1) and 0.5% adjuvant mixture. Dilutions from this stock solution are performed to allow for preparation of spray solutions consisting of single doses applied at a level equivalent to either 4.0, 1.0 or 0.25 kg/ha of active ingredient. The solutions are applied by a linear track sprayer set to deliver 1000 L/ha spray volume.

In pre-emergent studies, each dose of herbicide is applied as a band treatment over the seed zone. Pots containing the seeds are then top-dressed with soil, the plants are grown in the greenhouse and visually evaluated 7 and 19 days after treatment.

In post-emergence studies, each dose of compound is applied to the foliage of the selected weed seedling species. The plants are allowed to grow in the greenhouse and visually evaluated at 1, 7 and 19 days after treatment. Weed species tested are shown in Table 3. Some compounds of formula I showed activity in the pre-emergent and post emergent studies. Herbicidal control is evaluated as % injury with 100% injury considered complete control. At an application rate of 1.0 kg/ha active ingredient the compounds 1, 3, 5, 7-12, and 19-24 exhibited herbicidal control at greater than 80% for various tested weeds in both pre-emergence and post-emergence screenings.

In pre-emergence screening on grasses the compounds 60-65, 68, 71-78, 83, 84 and 94 provided greater than 75% control at 1.0 kg/ha on all tested weed species. It is understood that this list does not reflect all obtained data nor encompass all compounds which achieved the given limit.

TABLE 3

Common Name	Genus Species
Velvetleaf	Abutilon theophrasti
Redroot Pigweed	Amaranthus retroflexus
Mustard White	Sinapis alba
Black Nightshade	Solanum nigrum
Wild Oat	Avena fatua
Downy Brome	Bromus tectorum
Barnyardgrass	Echinochloa crus-galli
Green Foxtail	Setaria viridis

METHODS OF APPLICATION

Application of a compound of formula I is made according to conventional procedure to the weeds or their locus using a herbicidally effective amount of the compound, usually from 1 g to 10 kg/ha.

Compounds according to the invention may be used for the control of both broadleaf and grassy weeds in both preplant incorporation and pre- and post-emergent application. Compounds may also exhibit selectivity in various crops and may thus be suited for use in weed control in crops such as but not limited to corn, cotton, wheat, soybean and rice.

The optimum usage of a compound of formula I is readily determined by one of ordinary skill in the art using routine testing such as greenhouse testing and small plot field testing. It will depend on the compound employed, the desired effect (a phytotoxic effect requiring a higher rate than a plant growth regulating effect), the conditions of treatment and the like. In general, satisfactory phytotoxic effects are obtained when the compound of formula I is applied at a rate in the range of from 0.001 to 5.0 kg, more preferably of from 0.05 to 2.5 kg per hectare, especially 0.01 to 2.5 kg per hectare.

The compounds of formula I may be advantageously combined with other herbicides for broad spectrum weed control. Examples of herbicides which can be combined with a compound of the present invention include those selected from carbamates, thiocarbamates, chloroacetamides, triazines, dinitroanilines, benzoic acids, glycerol ethers, pyridazinones, uracils, phenoxys and ureas for controling a broad spectrum of weeds.

The compounds of formula I are conveniently employed as herbicidal compositions in association with agriculturally acceptable diluents. Such compositions also form part of the present invention. They may contain, aside from a compound of formula I as active agent, other active agents, such as herbicides or compounds having antidotal, fungicidal,

insecticidal or insect attractant activity. They may be employed in either solid or liquid forms such as a wettable powder, an emulsifiable concentrate, a granule or a microcapsule incorporating conventional diluents. Such compositions may be produced in conventional manner, for example by mixing the active ingredient with a diluent and optionally other formulating ingredients such as surfactants.

Agriculturally acceptable additives may be employed in herbicidal compositions to improve the performance of the active ingredient and to reduce foaming, caking and corrosion, for example.

The term "diluent" as used herein means any liquid or solid agriculturally acceptable material which may be added to the active constituent to bring it in an easier or improved applicable form, respectively, to a usable or desirable strength of activity. It can for example be talc, kaolin, diatomaceous earth, xylene or water.

"Surfactant" as used herein means an agriculturally acceptable material which imparts emulsifiability, spreading, wetting, dispersibility or other surface-modifying properties. Examples of surfactants are sodium lignin sulfonate and lauryl sulfate.

Particularly formulations to be applied in spraying forms such as water dispersible concentrates or wettable powders may contain surfactants such as wetting and dispersing agents, for example the condensation product of formaldehyde with naphthylene sulphonate, an ethoxylated alkylphenol and an ethoxylated fatty alcohol.

In general, the formulations include from 0.01 to 99% by weight of active agent and from 0 to 20% by weight of agriculturally acceptable surfactant, and from 0.1 to 99.99% of solid or liquid diluent(s) the active agent consisting either of at least one compound of formula I or mixtures thereof with other active agents. Concentrate forms of compositions generally contain between about 2 and 95%, preferably between about 10 and 90% by weight of active agent.

Typical herbicidal compositions, according to this invention, are illustrated by the following Examples A, B, C, D and E in which the quantities are in parts by weight.

EXAMPLE A

Preparation of a Soluble Powder

The water soluble salts of this invention can be hammer milled to a screen size of 100 mesh. The resulting powder will readily dissolve in water for spraying.

EXAMPLE B

Preparation of a Wettable Powder

25 Parts of a compound according to this invention are mixed and milled with 25 parts of synthetic fine silica, 2 parts of sodium lauryl sulphate, 3 parts of sodium lignosulfonate and 45 parts of finely divided kaolin until the mean particle size is about 5 micron. The resulting wettable powder is diluted with water to a desired concentration.

EXAMPLE C

Preparation of Water Dispersible Granule

40 Parts of a water insoluble parent acid compound according to this invention are wet milled in a solution of 10 parts MARASPERSE N-22 (a sodium lignosulfonate) and 50 parts water until a median particle size of 5 micron is reached. The slurry is spray dried on a NIRRO MOBILE MINOR unit at an inlet temperature of 150°C and outlet temperature of 70°C. The resulting granule can be readily dispersed in water for application.

EXAMPLE D

Preparation of a Microcapsule Suspension

(a) 0.38 Parts of a VINOL 205 (a partially hydrolyzed polyvinyl alcohol) are dissolved in 79.34 parts water.

(b) 3.75 Parts of an organic soluble parent acid compound according to this invention are dissolved in 3.75 parts TENNECO 500-100 (a xylene range aromatic solvent). To this

solution are added 0.63 parts of SEBACOYL CHLORIDE and 0.88 parts PAPI 135 (polymethylene isocyanate).

(c) 1.89 Parts piperazine and 0.50 parts of NaOH are dissolved in 12.60 parts of water.

Transfer premix (a) to a one quart osterizer and while stirring add premix (b) and sheer for approximately 60 seconds or until a droplet size of 10-20 microns is reached. Immediately add premix (c), continue stirring for 3 hours and neutralize with acetic acid. The resulting capsule suspension may be diluted in water for spraying.

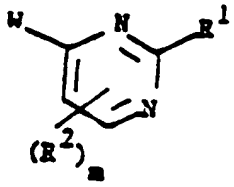
EXAMPLE E

Preparation of an Emulsifiable Concentrate

13 Parts of an organic soluble parent acid compound according to this invention are dissolved in 79 parts of TENNECO 500-100 along with 2 parts TOXIMUL RHF and 6 parts TOXIMUL S. TOXIMULS are a "matched pair"; each containing anionic and nonionic emulsifiers. The stable solution will spontaneously emulsify in water for spraying.

WHAT IS CLAIMED IS:

1. A compound of the formula



wherein W is a substituted phenyl or a substituted 5- or 6-membered aromatic heterocyclic ring wherein one or two atoms of said ring are selected from oxygen, nitrogen and sulfur; W being substituted by at least R;

R is CO_2R^4, CHO, $CONH\text{-}O\text{-}CH_2CO_2R^4$, $COSR^4$, $CO_2CHR^5OCOR^6$ or $CH{=}NOR^4$;

R^1 is Ar, $(Z)_xY\text{-}Ar$, and ZAr wherein Ar is an optionally substituted aryl or heteroaryl group selected from the group consisting of phenyl, pyridyl, piperonyl, naphthyl, indolyl, quinolyl, isoquinolyl, quinoxalinyl, quinazolinyl, benzoxazolyl, benzothiazolyl, phenanthryl, pyridyl-N-oxide, anthranilyl, pyrimidinyl, pyrazinyl, thienyl, furyl, pyrrolyl, oxazolyl, thiazolyl, isoxazolyl, isothiazolyl, imidazolyl, pyrazolyl, oxadiazolyl and thiodiazolyl; wherein the optional substituents are phenoxy, halo, alkyl, alkenyl, haloalkyl, haloalkylthio, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, haloalkoxy, alkoxyalkyl, cyano, nitro, alkoxycarbonyl, amino, alkylamino, dialkylamino or hydroxy; Y is O, S or NH; Z is optionally substituted C_1-C_3alkyl, C_2-C_4alkynyl, or an optionally substituted C_2-C_4alkenyl, wherein the substituents are independently alkyl and halogen;

x is 0 to 2;

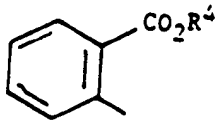
R^2 is independently hydrogen, halogen, alkyl, alkenyl, haloalkyl, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, alkoxyalkyl, cyano, nitro, amino, alkylamino, dialkylamino, CO_2R^4 or hydroxy;

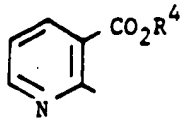
m is 1 to 2;

R^4 is hydrogen, alkali or alkaline earth cation, ammonium cation, substituted ammonium cation, phosphonium cation, alkyl phosphonium cation, trialkylsulfonium cation, trialkylsulfoxonium cation, alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl or optionally substituted phenylalkyl;

R^5 is hydrogen or alkyl; and

R^6 is alkyl, alkenyl, haloalkyl, alkoxyalkyl, optionally substituted phenyl or optionally substituted phenylalkyl and provided that (i) when R^1 is phenyl; W is not

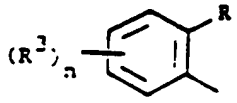
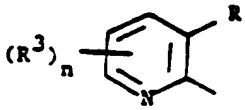
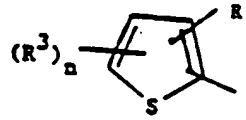
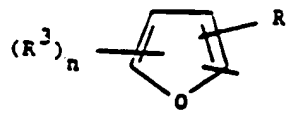
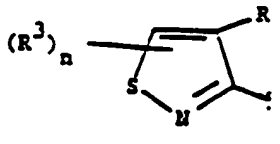


and (ii) when R^1 is optionally substituted phenyl and W is 

R^2 is not alkyl or alkenyl.

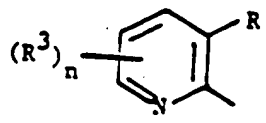
2. A compound according to Claim 1 wherein W is phenyl, pyridyl, thienyl, furyl or isothiazolyl.

3. A compound according to Claim 2 wherein W is





and


wherein R^3 is independently hydrogen, halogen, alkyl, haloalkyl, alkoxy, cyano, alkoxycarbonyl, alkylamino, dialkylamino, and $-N(R^5)-CO-R^6$, and n is 1 to 4.

4. A compound according to Claim 3 wherein W is



;

R is CO_2R^4; CHO; $CONH\text{-}O\text{-}CH_2CO_2R^4$; $COSR^4$; $CO_2CHR^5OCOR^6$ or $CH{=}NOR^4$;

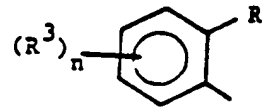
R^1 is Ar, Z_xYAr or ZAr wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl, anthranilyl or phenanthryl;

R^2 is hydrogen, CO_2R^4 and alkoxy; and

R^3 is hydrogen and halogen.

5. A compound according to Claim 4 wherein R is $CO_2CHR^5OCOR^6$ or CO_2R^4; R^4 is hydrogen, Na, NH_4, K, Ca, Mg, trimethylsulfonium, trimethyl sulfoxonium and isopropylammonium, R^1 is optionally substituted phenyl, pyridyl, naphthyl, piperonyl, quinolyl, (Z)phenyl, or $(Z)_x$Ophenyl; Z is C_1-C_3alkyl, C_2-C_4alkynyl or C_2-C_4alkenyl and x is 1.

6. A compound according to Claim 3 wherein W is



;

R is CO_2R^4; CHO; $CONH\text{-}O\text{-}CH_2CO_2R^4$; $COSR^4$; $CO_2CHR^5OCOR^6$ or $CH{=}NOR^4$;

R^1 is Ar, Z_xYAr or ZAr wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl, anthranilyl or

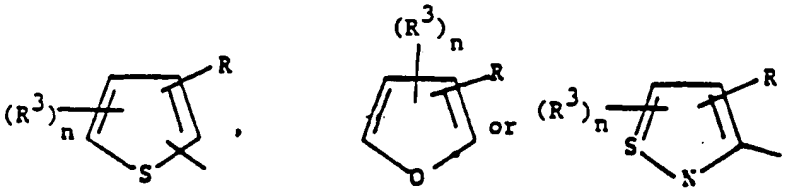
phenanthryl;

R^2 is hydrogen, alkyl, CO_2R^4, and, alkoxy; and

R^3 is hydrogen and halogen.

7. A compound according to Claim 4 wherein R is $CO_2CHR^5OCOR^6$ or CO_2R^4; R^4 is hydrogen, Na, NH_4, K, Ca, Mg, trimethylsulfonium, trimethyl sulfoxonium and isopropylammonium; R^2 is hydrogen and R^1 is optionally substituted phenyl, pyridyl, naphthyl, piperonyl, quinolyl, (Z)phenyl, or $(Z)_x$Ophenyl and x is 1.

8. A compound according to Claim 3 wherein W is



R is CO_2R^4; CHO; CONH-O-$CH_2CO_2R^4$; $COSR^4$; $CO_2CHR^5OCOR^6$ or $CH{=}NOR^4$;

R^1 is Ar, Z_xOAr or ZAr wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl or phenanthryl;

R^2 is hydrogen; and

R^3 is hydrogen and halogen.

9. A compound according to Claim 3 wherein

R is CO_2R^4;

R^4 is hydrogen, Na, NH_4, K, Ca, Mg, trimethylsulfonium, trimethylsulfoxonium or

isopropylammonium;

R^1 is Ar, $(Z)_xY$-Ar and ZAr wherein Ar is an optionally substituted phenyl, pyridyl, naphthyl, indolyl, piperonyl, quinolyl, benzoxazolyl, benzothiazolyl, anthranilyl or phenanthryl wherein the optional substituents are halo, alkyl, alkenyl, haloalkyl, alkylthio, alkylsulfinyl, alkylsulfonyl, alkoxy, haloalkoxy, alkoxyalkyl, cyano, nitro, alkoxycarbonyl, amino, alkylamino, dialkylamino and hydroxy; Y is O, S or NH; Z is an optionally substituted C_1-C_3alkyl, C_2-C_4alkynyl, or an optionally substituted C_2-C_4 alkenyl wherein the substituents are independently alkyl and halogen; and x is 0 to 2.

10. A herbicidal composition comprising a herbicidally effective amount of a compound of Claim 1 in association with an agriculturally acceptable diluent.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 95/00086

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07D401/04 A01N43/54 C07D401/14 C07D405/04 C07D239/24
C07D417/04 C07D409/04 C07D405/14 C07D417/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 752 324 (THOMAS) 21 June 1988 cited in the application see claim 1 ---	1-10
X	BIOCHEM. INT., vol. 1982, 1982 pages 431-438, PRYOR ET AL 'Purification of maize alcohol dehydrogenase and competitive inhibition by pyrazoles.' Compound 20 on page 435 --- -/--	1-10

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
30 May 1995	13. 06. 95

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Gettins, M

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	AUST J.CHEM., vol. 32, 1979 pages 669-679, HARRIS ET AL 'Synthetic Plant Growth Regulators' cited in the application Compound 4 on page 669	1-10
X	DE,A,40 31 798 (HOECHST) 9 April 1992 cited in the application see claim 1	1-10
A	EP,A,0 484 750 (BAYER AG) 13 May 1992 see claim 1	1-10

INTERNATIONAL SEARCH REPORT

:ormation on patent family members

Interna al Application No
PCT/EP 95/00086

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4752324	21-06-88	DE-A- 3623302	14-05-87
		EP-A- 0222254	20-05-87
		JP-A- 62120382	01-06-87
DE-A-4031798	09-04-92	NONE	
EP-A-484750	13-05-92	DE-A- 4035141	07-05-92
		JP-A- 4283578	08-10-92